Durability Improvements Through Degradation Mechanism Studies

Fuel Cell Technologies
2009 Kickoff Meeting

September 30-October 1, 2009
DOE Forrestal Building

Presented by: Rod Borup
LANL: Rangachary Mukundan, John Davey, Andrea Labouriau, Roger Lujan, Bo Li, Dusan Spernjak
ANL: Rajesh Ahluwalia, Xiaohua Wang
Ballard: Sylvia Wessel, Paul Beattie, Greg James, Daniel Ramrus, Svetlana Loif, Warren Williams
Ion Power: Steve Grot, Walter Grot
LBNL: Adam Weber
ORNL: Karren More, Mike Brady
UNM: Kateryna Artyushkova, Plamen Atanassov

This presentation does not contain any proprietary or confidential information
Organizations / Partners

- Los Alamos National Lab (LANL)
  - Lead: durability testing and fundamental characterization
- Argonne National Laboratory (ANL)
  - Integrated comprehensive degradation model and model distribution
- Ballard Power Systems (BPS)
  - Fuel cell system testing, stack integration, component interactions, and stack materials
- Ion Power
  - Specialized membranes, Ionomer and MEAs
- Lawrence Berkeley National Laboratory (LBNL)
  - Fundamental modeling
- Oak Ridge National Laboratory (ORNL)
  - Characterization (TEM) and metal bipolar plates
- University of New Mexico (UNM)
  - Characterization (XPS) and carbon corrosion measurements
## Budget

### DOE Cost Share vs. Recipient Cost Share

<table>
<thead>
<tr>
<th>DOE Cost Share</th>
<th>Recipient Cost Share</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8,225,000</td>
<td>$501,263</td>
<td>$8,726,263</td>
</tr>
<tr>
<td>94%</td>
<td>6%</td>
<td>100%</td>
</tr>
</tbody>
</table>

### YR 1, YR 2, YR 3, YR 4, CUMULATIVE

<table>
<thead>
<tr>
<th>YR 1</th>
<th>YR 2</th>
<th>YR 3</th>
<th>YR 4</th>
<th>CUMULATIVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2000k</td>
<td>$2000k</td>
<td>$2175k</td>
<td>$2050k</td>
<td>$8225k</td>
</tr>
</tbody>
</table>

### FY09-10 (Year 1)

<table>
<thead>
<tr>
<th>Source</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANL</td>
<td>$725k</td>
</tr>
<tr>
<td>Industrial + Univ. Partners (Ballard, Ion Power, UNM)</td>
<td>$425k</td>
</tr>
<tr>
<td>Other National Labs (ANL, LBNL, ORNL)</td>
<td>$850k</td>
</tr>
<tr>
<td>FY09-FY10 Total</td>
<td>$2000k</td>
</tr>
</tbody>
</table>
Objectives

• Identification and delineation of individual component degradation mechanisms
• Development of advanced in situ and ex situ characterization techniques for analysis of fuel cell component degradation
• Quantify the influence of inter-relational operating environment between different fuel cell components
• Degradation measurements of components and component interfaces
• Elucidation of component interactions, interfaces, operating conditions leading to cell degradation
• Individual degradation models of all fuel cell components
• Development and public dissemination of an integrated comprehensive model of cell degradation
• Methods to mitigate degradation of components
### Technical Targets/Barriers

#### Table 3.4.3 Technical Targets: 80-kWₑ (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2003 Status</th>
<th>2005 Status</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durability with cycling</td>
<td>hours</td>
<td>N/A</td>
<td>2,000</td>
<td>5,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Transient response (time for 10% to 90% of rated power)</td>
<td>seconds</td>
<td>&lt;3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Unassisted start from low temperature</td>
<td>ºC</td>
<td>N/A</td>
<td>-20</td>
<td>-40</td>
<td>-40</td>
</tr>
</tbody>
</table>

#### Table 3.4.5 Technical Targets: Stationary PEM Fuel Cell Stack Systems (5-250 kW) Operating on Reformate

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2005 Status</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durability</td>
<td>hours</td>
<td>20,000</td>
<td>40,000</td>
</tr>
<tr>
<td>Survivability (min and max ambient temperature)</td>
<td>ºC</td>
<td>-25</td>
<td>-35</td>
</tr>
<tr>
<td></td>
<td>ºC</td>
<td>+40</td>
<td>+40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Durability</th>
<th>Hours</th>
<th>5,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start /Stop Cycles</td>
<td></td>
<td>17,000</td>
</tr>
<tr>
<td>Frozen</td>
<td></td>
<td>1,650</td>
</tr>
<tr>
<td>Load Cycles</td>
<td></td>
<td>1,200,000</td>
</tr>
</tbody>
</table>
Degradation Mechanism Studies Timeline

Project initiated in September 2009 for 4 years

| Task Timeline Schedule: Quarters (Q) with Milestones (M) and Decision Points (G) |
|---------------------------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Q Task                          | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 1a (i) (Ion Pr/LANL)            |   |   |   |   |   |   |   |  M | G |   |   |   |   |   |   |   |
| 1a (ii - iv) (LANL)             |   |   |   |   |   |   |   | M  | M | G |   |   |   |   |   |   |   |
| 1a (v - vi) (BPS)               |   | G | M | M | M | M | M | M | M |   |   |   |   |   |   |   |
| 1b (LANL)                       |   | M | M | M | M | M | M | M | M |   |   |   |   |   |   |   |
| 1c (LANL)                       |   |   | M | G | M | M | M | M | M |   |   |   |   |   |   |   |
| 1d (UNM / LANL)                 |   | M | M | M | M | M | M | M | M |   |   |   |   |   |   |   |
| 2a (LANL)                       |   |   | M | M | M | M | M | M | M |   |   |   |   |   |   |   |
| 2b (LANL)                       |   |   | M | M | M | M | M | M | M |   |   |   |   |   |   |   |
| 2c (LANL)                       |   |   | M |   | M | M | M | M | M |   |   |   |   |   |   |   |
| 3a – b (LANL)                   |   |   | M |   |   | M | M | M | M |   |   |   |   |   |   |   |
| 3c – g (LANL)                   |   |   | M | M | G | M | M | M | M |   |   |   |   |   |   |   |
| 4a (LBNL)                       |   |   |   |   |   |   |   | M |   |   |   |   |   |   |   |   |   |
| 4b (LBNL)                       |   |   |   |   |   |   |   | M |   |   |   |   |   |   |   |   |   |
| 4c (LBNL)                       |   |   |   |   |   |   |   | M |   |   |   |   |   |   |   |   |   |
| 5a (ANL)                        |   |   |   |   |   |   |   | M |   |   |   |   |   |   |   |   |   |
| 5b (ANL)                        |   |   |   |   |   |   |   | M |   |   |   |   |   |   |   |   |   |
| 5c (ANL)                        |   |   |   |   |   |   |   | M |   |   |   |   |   |   |   |   |   |
| 5d (ANL)                        |   |   |   |   |   |   |   | M | G | M |   |   |   |   |   |   |   |
Degradation Mechanism Studies Timeline

Project Timeline

Begin 08/09

<table>
<thead>
<tr>
<th>M1</th>
<th>G1</th>
<th>Q4</th>
<th>M2</th>
<th>Q6</th>
<th>M3</th>
<th>G2</th>
<th>Q8</th>
<th>G3</th>
<th>Q10</th>
<th>M4</th>
<th>M5</th>
<th>G4</th>
<th>Q12</th>
<th>M6</th>
<th>Q16</th>
<th>End 09/13</th>
</tr>
</thead>
</table>

Single Component Degradation Studies

Multi-component Degradation Studies

Parametric Aging Studies

Comprehensive Cell Degradation Models

Science-Based Degradation Models

Development of *in situ* Analytical Techniques

Mitigation Strategies

Milestones:

**M1**: LANL/UNM: Definition of surface functional groups on aged GDLs

**M2**: LANL/BPS: Identification of component impurities from seals and bipolar plates

**M3**: Ion Power/LANL: RH/potential effect on chemical and mechanical stabilized ionomers.

**M4**: LANL: Completion of drive cycle (load) life testing with start-up/shut-down

**M5**: ANL: Completion of individual degradation models

**M6**: ANL: Distribution of integrated cell degradation model.

Go/No-Go

**G1**: ORNL: Go/No Go Decision: Plate Resin analysis depending upon acceptable agreement (analysis).

**G2**: Ion Power/LANL: RH/potential effect on chemical and mechanical stabilized ionomers. Go/No Go: If no new degradation mechanisms over 1000 hrs – conclude membrane AST testing

**G3**: LANL: X-Ray Tomography to provide resolution ~ < 1 micron pore changes. Go/No: If not able to detect changes in microstructure: conclude the Tomography imaging.

**G4**: LANL: *in situ* XRD comparison of Pt vs. PtCo ripening. - Go/No Go Decision: EXAFS comparison of Pt vs PtCo
Task Outline

• Task 1. Elucidation of Single Component Degradation Mechanisms
  – Task 1a: Single Component Degradation Studies
  – Task 1b: Single Component Interaction Effects
  – Task 1c: Microstructure Impact on Durability
  – Task 1d: Carbon Degradation (Catalyst Support, GDL/MPL, Bipolar Plates)

• Task 2. Elucidation of Multi-component Degradation Mechanisms
  – Task 2a: Multi-component studies (full cell degradation testing)
  – Task 2b: Multi-component studies
  – Task 2c: Component interface studies

• Task 3: Parametric Aging Studies

• Task 4: Science-Based Degradation Models
  – Subtask 4a: Electrocatalyst Degradation
  – Subtask 4b: Membrane-Related Cation Degradation Mechanisms
  – Subtask 4c: Liquid-Enhanced Degradation Mechanisms

• Task 5: Comprehensive Cell Degradation Models

• Task 6: Development of *in situ* Analytical Techniques and Mitigation Strategies

Components Include: Membrane and Ionomer, Catalyst, Catalyst support, Gas Diffusion Layer and Microporous Layer GDL/MPL, Bipolar Plate (Metal & Carbon Based), Seal Materials
Degradation Mechanism Studies
Approach

- Fuel cell testing
  - Individual component testing
    - (including controlled environmental aging)
  - Measurements of degradation

- Characterization
  - Chemical characterization of components
  - Morphological evaluation of components using SEM and TEM.
  - Physical characterization using Hg and H₂O porosimetry, surface energy analysis, contact angle, BET surface area, pore size, pore volume.

- Modeling
  - Fundamental degradation mechanisms (LBNL)
  - Individual degradation models – kinetic/rate based (ANL)
  - Integrated comprehensive model (ANL)
Characterization Methods to Delineate Degradation Mechanisms

- TEM (Transmission Electron Microscopy)
- X-ray Tomography - Xradia MicroXCT
- Powder XRD (x-ray diffraction)
- SEM/ESEM (Environmental Scanning Electron Microscopy)
- FTIR (ATR, Transmission, DRIFTS)
- Laser Ablation ICP-MS
- XPS – (X-ray Photoelectron Spectroscopy)
- NMR (Solid-state and solution)
- IGC - (Inverse Gas Chromatography)
- TGA/DSC & MS (Thermogravametric Analysis / Differential Scanning Calorimetry)
TEM of Catalyst Particle Growth (ORNL)

X-Ray Diffraction of Ionomer Crystalization (LANL)

XPS of Carbon Surface Species (UNM)

18 degree peak is used to determine crystallinity of Nafion.

Hydrophobicity Measurements

Unaged #1

Aged
Any inputs/needs

- OEM input on realistic shut-down/start-up protocols and other operating conditions